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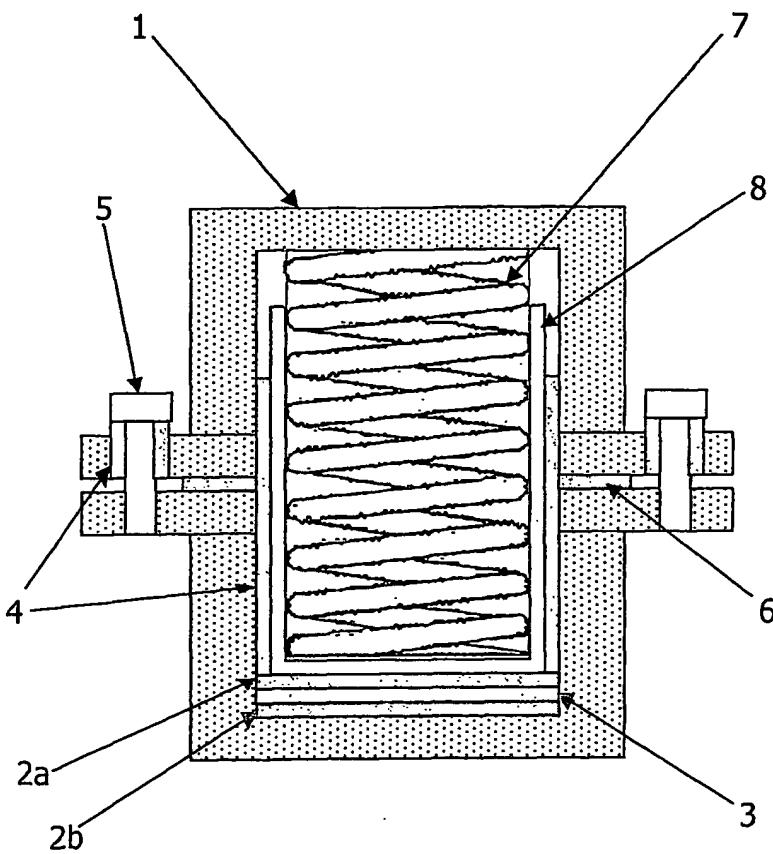
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(54) Title: ENERGY STORAGE DEVICES



(57) Abstract: Pyrrolidinium based room temperature ionic liquids, and phosphorous and arsenic analogues, are used as electrolytes in energy storage devices including secondary lithium batteries, supercapacitors and asymmetric battery-supercapacitors. The electrolytes preferably contain lithium ions as the charge-carrying species. The electrolytes are in a liquid state at the operating temperature.

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ENERGY STORAGE DEVICES

This invention relates to the application of pyrrolidinium based room temperature ionic liquids as electrolytes in 5 energy storage devices such as secondary lithium batteries. The present invention further relates to energy storage devices, and particularly secondary lithium batteries, containing the electrolyte.

10 Background to the Invention

Lithium rechargeable batteries (i.e. secondary lithium batteries, in which lithium ions are the principal charge carriers) are important devices in the field of energy 15 storage. They offer advantages over other secondary battery technologies due to their higher gravimetric and volumetric capacities as well as higher specific energy.

Secondary lithium batteries fall into two classes - those 20 in which the negative electrode is lithium metal, known as a "lithium metal battery", and those in which the negative electrode is comprised of a lithium intercalation material, known as "lithium - ion batteries". In terms of specific energy and power, lithium metal is the preferred 25 negative electrode material. However, when 'traditional' solvents are used in combination with lithium metal negative electrodes, there is a tendency for the lithium metal electrode to develop a dendritic surface [1]. The dendritic deposits limit cycle life and present a safety 30 hazard due to their ability to short circuit the cell - potentially resulting in fire and explosion. These shortcomings have necessitated the use of lithium intercalation materials as negative electrodes (creating the well-known lithium-ion technology), at the cost of 35 additional mass and volume for the battery.

Researchers have continued to search for a solution to the

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- poor cycling characteristics of the lithium metal electrode - notably through the use of polymer electrolytes. However lithium ion motion in polymer electrolytes is mediated by segmental motions of the
- 5 polymer chain leading to relatively low conductivity. The low conductivity and low transport number of the polymer electrolytes has restricted their application in practical devices.
- 10 Alternative solvents such as 1,3 dioxolane have been trialled with some success (i.e. uniform lithium deposition morphology) but have been found to react with lithium during cycling of the battery - thus the electrolyte eventually dries out and the battery fails
- 15 prematurely [2].

In another field, since their first observation in 1927, various parties have studied room temperature ionic liquids (RTILs) and their potential applications. Room

20 temperature ionic liquids are organic ionic salts having a melting point below the boiling point of water (100°C). Accordingly, within this class are organic ionic salts that are liquid over a wide temperature range, typically from below room temperature to above 200°C.

25 Room temperature ionic liquids have been known for a long time, although those studied before 1992 were moisture sensitive, which hampered the development of practical applications. In 1992 the first air and moisture stable

30 ionic liquids were reported, and since then a large number of anion-cation combinations have been developed.

However, compared to other solvent systems, published research pertaining to the use of room temperature ionic

35 liquids in lithium secondary batteries is sparse. Few, if any, of the systems proposed have been demonstrated to be capable of use in practice. Some systems reported contain

air and moisture sensitive room temperature ionic liquids. Research on other systems indicates that the battery would have insufficient cycling efficiency or would be subject to severe limits on the possible charging/discharging rates. Other publications specify that the room temperature ionic liquids must be used in the solid phase. Moreover, little work if any has been reported to show whether the proposed systems enable lithium to be both taken up by the negative electrode, and importantly then released. Unless this is achievable, and demonstrated, it cannot be predicted the electrolyte will have utility in a secondary battery application.

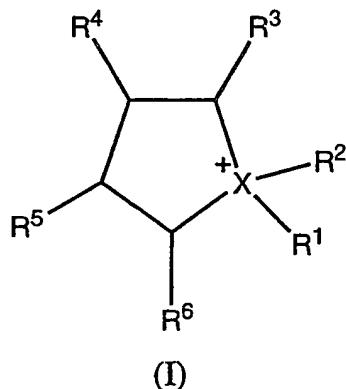
Description of the Invention:

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According to the present invention there is provided an electrolyte for use in an energy storage device, the electrolyte comprising a room temperature ionic liquid of:

(i) a cation of Formula I:

20



in which X is N, P or As

R¹ is alkyl or a fully or partially halogenated alkyl;

R² is alkyl or a fully or partially halogenated alkyl;

25 R³ to R⁶ are each independently H, alkyl, halo, fully or partially halogenated alkyl, nitrile, alkyl substituted by nitrile or heteroatom, or any other group; and

(ii) an anion;

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together with
(iii) lithium ions.

It has been demonstrated in the present application that
5 the described room temperature ionic liquid (RTIL)
electrolytes provide uniform deposition of lithium metal
onto an electrode (i.e. provide uniform lithium deposition
morphology), together with good release of lithium back
10 into the electrolyte, resulting in cycling of lithium at
high efficiency. In addition the electrolyte is
nonvolatile and nonflammable.

The electrolyte may comprise one or more further
components, including one or more further room temperature
15 ionic liquids, one or more solid electrolyte interphase-
forming additives; one or more gelling additives;
counterions to the lithium ions which are either the same
as or different to the anions of the room temperature
ionic liquid; and organic solvents. Consequently,
20 references to "a" cation or "an" anion should be
interpreted broadly to encompass one or more of each of
these.

Solid electrolyte interphase-forming additives are shown
25 to improve the deposit morphology and efficiency of the
lithium cycling process. The gelling additives provide a
gel material while retaining the conductivity of the
liquid. This offers specific benefits over liquids in that
it will enable fabrication of a flexible, compact,
30 laminated device free from leakage and capable of
construction with varying geometry.

The electrolytes of the present invention are liquid at
their intended use temperature, and have characteristics
35 that make them suitable for use in energy storage devices,
such as secondary lithium batteries, and particularly
lithium metal batteries. The electrolytes have high

- 5 -

stability towards lithium, and provide long cycle life with a lithium metal electrode.

Consequently, the present invention also provides energy 5 storage devices, such as secondary lithium batteries comprising the electrolyte as described above.

In general terms, the secondary lithium battery may comprise:

10 a battery case;
battery terminals;
a negative electrode;
a positive electrode;
a separator for separating the negative electrode from the
15 positive electrode; and
the electrolyte as described herein.

In the case where both positive and negative electrodes include Li - intercalation materials, the battery is 20 referred to as a lithium-ion battery.

The characteristics of the electrolytes also make them suitable for use in supercapacitors and asymmetric battery-supercapacitors. The present application also 25 provides such devices containing the electrolyte as described herein.

The present application further provides for the use of the room temperature ionic liquids described above as 30 electrolytes for energy storage devices in which the electrolyte is liquid at the temperature of use of the device.

Suitable methods for charging and conditioning the energy 35 storage devices, batteries or cells to improve the cycling rate and cycle life of the devices, batteries or cells have also been identified. The charging method comprises

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charging, for at least a part of the charging stage (i.e. for at least 5 minutes), at a charge rate of less than 0.25 mAcm⁻². The conditioning method comprises the steps of discharging and recharging the device, battery or cell, 5 wherein the recharging is conducted at a rate of less than 0.25 mAcm⁻² for at least a part of the recharging stage.

The present invention further provides a method for preparing an electrolyte, comprising adding lithium ions 10 in the form of a salt to said room temperature ionic liquid, mixing and drying under vacuum at elevated temperature.

Brief Description of the Figures

15 Figure 1 is a schematic view of a battery-like cell in accordance with one embodiment of the invention.

20 Figure 2 is a schematic view of a 3-electrode cell used to conduct testing of the electrolytes.

Figure 3 is a cyclic voltammogram for a cell containing the electrolyte of one embodiment of the invention as described in Example 1.

25 Figure 4 is a graph of the cycling efficiency of Example 2 conducted at 0.25 mAcm⁻² and 0.25/1 Ccm⁻² on Pt at 50°C.

30 Figure 5 is a graph of the cycling efficiency of Example 3 conducted at 1.0 mAcm⁻² and 0.25/1 Ccm⁻² on Pt at 50°C.

Figure 6 is a plot showing cycling efficiency of Example 4 conducted at 0.25 mAcm⁻² on Pt and 0.25/1 Ccm⁻² at 50°C.

35 Figure 7 is a graph of the cycling efficiency of Example 5 conducted at 0.25 mAcm⁻² and 0.25/1 Ccm⁻² on Cu at 50°C.

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Figure 8 is a graph of the cycling efficiency of Example 6 conducted at 0.1 mAcm^{-2} and $0.25/1 \text{ Ccm}^{-2}$ on Cu at 50°C , with section a) showing the first 30 cycles, b) cycles 150-180 and c) cycles 300-330.

5

Figure 9 is graph of the cycling efficiency of Example 7 performed at increased current density as compared with Example 6, with section a) showing 0.25 mAcm^{-2} and b) 0.5 mAcm^{-2} .

10

Figure 10 is a graph of the cycling efficiency of Example 8 conducted at 1.0 mAcm^{-2} and $0.25/1 \text{ Ccm}^{-2}$ on Pt at 50°C .

15

Figure 11 is a graph demonstrating the charge against cell voltage of the cell described in Example 10.

Figure 12 is a graph demonstrating the charge against cell voltage of the cell described in Example 11.

20

Figure 13 is a graph demonstrating the charge against cell voltage of the cell described in Example 12.

25

Figure 14 is a graph of the electrochemical window for a phosphorous-based room temperature ionic liquid as described in Example 13.

Detailed Description of the Invention

30

The features of embodiments of the present invention will now be described in further detail.

Room temperature ionic liquids

Room temperature ionic liquids (RTILs) are organic ionic salts having a melting point below the boiling point of water (100°C). The RTILs of the present application need to have a melting point such that the ionic salt will be in liquid form at the temperature of operation of the

device. Those having melting points of 10°C or less are preferred. The liquid form is necessary to provide high enough conductivity. Use of RTILs that are solid at the operating temperature are not sufficiently conductive.

5

In the context of the present application, the term "liquid" is used broadly to encompass gels, which have conductivity similar to liquids, but not to solids.

10 In addition to the high conductivity, the RTILs possess a wide electrochemical window, high thermal stability, low safety hazards (non-flammable, non-volatile), and low toxicity. The salts obtain their liquid character from the properties of the anions and cations of which they are
15 comprised.

The factors which contribute to the liquid nature of the RTIL are well described in the literature: J. D. Holbrey and K. R. Seddon, *Clean Products and Processes*, 1, 0223
20 (1999); P. Bonhote, A. P. Dias, N. Papageorgiou, M. Armand, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, 35, 1168 (1996).

Pyrrolidinium cation

25 The term "pyrrolidinium cation" refers to cations of formula I, of the general pyrrolidinium structure, or derivatives thereof which may not strictly be considered to be "pyrrolidiniums". Examples of such derivatives are the phosphorous based analogues described below.

30

The cations of Formula I encompassed by the present application fall into a number of subclasses. Before describing these subclasses, we provide further explanation of the terms used in Formula I.

35

The term "alkyl" is used in its broadest sense to refer to any straight chain, branched or cyclic alkyl groups of

from 1 to 20 carbon atoms in length and preferably from 1 to 10 atoms in length. The term encompasses methyl, ethyl, propyl, butyl, s-butyl, pentyl, hexyl and so forth. The alkyl chain may also contain hetero-atoms, a halogen, a 5 nitrile group, and generally other groups or ring fragments consistent with the substituent promoting or supporting electrochemical stability and conductivity.

Halogen, halo, the abbreviation "Hal" and the like terms 10 refer to fluoro, chloro, bromo and iodo, or the halide anions as the case may be.

R3, R4, R5 and R6 can be any of the groups identified above, but is most suitably H or halo (based on the fact 15 that the pyrrolidinium cation may be partially or fully halogenated, as described in further detail below). The expression "any other group" encompasses any substituent or ring fragment consistent with the substituent promoting or supporting electrochemical stability and conductivity.

20 R1 is preferably methyl, or partially or fully halogenated methyl (based on the fact that the pyrrolidinium cation may be partially or fully halogenated, described below). It will be understood that R1 cannot generally be H, as 25 this may result in reduced electrochemical stability.

X may be N, in which case the cation is a pyrrolidinium cation, or it may be P, in which case the cation is the phosphonium salt. On the basis of its availability N is 30 typically used, although the function of the phosphonium analogue can be predicted to be very similar to that of the pyrrolidinium cation. Similarly, X may be As, in which case an arsolanium analogue is obtained.

35 The cation of Formula I may be partly or fully halogenated. Chemical modification of this class of cations is a well-explored field, and is known to be a

- 10 -

suitable technique for modifying the electrochemical stability and conductivity of the cation. It also impacts on the melting point of the ionic salt of the cation and anion, thus enabling a selection of a suitable ionic salt
5 having the necessary melting point to be made.

The fluorinated cation may in some cases be obtained by alkylation of a suitable perfluorinated precursor (e.g., from a perfluorinated pyrrolidine), which can be obtained
10 from commercial source. Alternatively, a perfluoroalkyl substituted pyrrolidinium can be obtained by the reaction of a suitable perfluorinated alkyl halide with pyrrolidine as demonstrated by Singh et al.¹ Other methods allowing direct fluorination of the RTIL electrolyte can also be
15 applied.²

References

1. R. P. Singh, S. Manandhar and J. M. Shreeve, *Tetrahedron Lett.*, 43, 9497 (2002).
2. M. Kobayashi, T. Inoguchi, T. Iida, T. Tanioka, H. Kumase and Y. Fukai, *J. Fluorine Chem.*, 120, 105 (2003).

The identity of R₂ can impact significantly on the melting point of the room temperature ionic liquid. R₂ is preferably an alkyl of 2 or more carbon atoms, more
25 preferably three or more carbon atoms, and is suitably iso-propyl or an alkyl of 4 or more carbon atoms. When R₂ is butyl, the melting point is most appropriate for standard ambient temperature applications (eg 10 - 25°C), whereas shorter carbon chain lengths in this position tend
30 to lower the melting point, making the electrolyte only suitable for higher temperature applications.

Conventional devices stop operating at higher temperatures. Thus, the use of the defined room
35 temperature ionic liquids in electrolytes which are capable of functioning at higher temperatures, or lower temperatures, depending on the selection of the

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substituents on the cation, provides a significant advance over the prior art. By suitable choice of the electrolyte components, the device may operate in the temperature range of from -30°C to 200°C. Lower end temperature devices would suitably operate in the 0-50°C region, and higher temperature devices in the 40°-150°C region.

The bis(trifluoromethylsulfonyl)amide salts of N-ethyl N-methyl pyrrolidinium bis(trifluoromethylsulfonyl)amide melt at 86°C, N-propyl N-methyl pyrrolidinium bis(trifluoromethylsulfonyl)amide at 13°C and N-butyl N-methyl pyrrolidinium bis(trifluoromethylsulfonyl)amide at -18°C, in the absence of Li salt or other additives. The melting points vary with additives, but are most often lower. Thus, the appropriate cation can be selected to provide an electrolyte composition that is liquid and has the required stability and cycle life for a given application, at a given temperature range.

20 **Anion**

The term "anion" is used broadly to refer to any organic or inorganic anion forming a salt with the cation. The choice of anion is principally based on the salt of the anion and the cation being liquid at the intended use temperature. In addition, the choice of anion will be based upon the anion having sufficient electrochemical stability for the chosen electrodes of the energy storage device.

30

The anion associated with the cation(s) may for instance be selected from one or more of the following:

- (i) BF_4^- and perfluorinated alkyl fluorides of boron. Encompassed within the class are anions of the formula $\text{B}(\text{C}_x\text{F}_{2x+1})_a\text{F}_{4-a}^-$ where x is an integer between 0 and 6, and a is an integer between 0 and 4.
- (ii) Halides, alkyl halides or perhalogenated alkyl

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halides of group VA(15) elements. Encompassed within this class are anions of the formula $E(C_xY_{2x+1})_a(Hal)_{6-a}^-$ where a is an integer between 0 and 6, x is an integer between 0 and 6, y is F or H, and E is P, As, Sb or Bi. Preferably 5 E is P or Sb. Accordingly this class encompasses PF_6^- , SbF_6^- , $P(C_2F_5)_3F_3^-$, $Sb(C_2F_5)_3F_3^-$, $P(C_2F_5)_4F_2^-$, AsF_6^- , $P(C_2H_5)_3F_3^-$ and so forth.

(iii) $C_xY_{2x+1}SO_3^-$ where x = 1 to 6 and y = F or H. This class encompasses $CH_3SO_3^-$ and $CF_3SO_3^-$ as examples.

10 (iv) sulfonyl amides, including the bis amides and perfluorinated versions thereof. This class includes $(CH_3SO_2)_2N^-$, $(CF_3SO_2)_2N^-$ (also abbreviated to Tf₂N) and $(C_2F_5SO_2)_2N^-$ as examples. The bis amides within this group may be of the formula $(C_xY_{2x+1}SO_2)_2N^-$ where x = 1 to 6 and y = F or H.

15 (v) $C_xF_{2x+1}COO^-$, including CF_3COO^-

(vi) sulfonyl and sulfonate compounds, namely anions containing the sulfonyl group SO₂, or sulfonate group SO₃⁻ not covered by groups (iii) and (iv) above. This class 20 encompasses aromatic sulfonates containing optionally substituted aromatic (aryl) groups, such as toluene sulfonate and xylene sulfonate

(vii) cyanamide compounds and cyano group containing anions, including cyanide, dicyanamide and tricyanomethide

25 (viii) Succinamide and perfluorinated succinamide

(ix) Ethylendisulfonylamide and its perfluorinated analogue

(x) SCN⁻

30 (xi) Carboxylic acid derivatives, including $C_xH_{2x+1}COO^-$ where x is as defined above

(xii) Weak base anions

(xiii) Halide ions such as the iodide ion

Amongst these anions, the preferred classes are those 35 outlined in groups (i), (ii), (iii), (iv) and (vi) above.

However, should they be disclosed in the prior art,

according to one particular embodiment, where the room temperature ionic liquid contains only one type of cation of Formula I with that cation being N-methyl-N-ethylpyrrolidinium or N-methyl-N-propylpyrrolidinium, and

5 the electrolyte contains no additives, the anion is selected to be other than $\text{N}(\text{CF}_3\text{SO}_2)_2^-$, CF_3SO_3^- , $\text{N}(\text{C}_2\text{F}_5\text{SO}_2)_2^-$, BF_4^- and PF_6^- . These specific room temperature ionic liquids are typically more solid or waxy at lower temperatures.

In contrast, room temperature ionic liquids based on N-

10 methyl-N-butylpyrrolidinium as the single cation of Formula I have a lower melting point and are demonstrated to operate well in the applications described herein, even without additives.

15 *Description of Abbreviations used to Name Compounds*

In the following description and claims, abbreviations are used to name the compounds. For cations of Formula I containing N as the atom X (ie pyrrolidinium-based cations), the prefix P is used. Two numbers follow this

20 to refer to the number of carbon atoms of each of the substituents; thus P13 refers to the methyl propyl pyrrolidinium cation. Some anions are also commonly referred to by abbreviations, with one notable one used below being Tf, used to refer to trifluoromethylsulfonyl;

25 with the result that $(\text{Tf})_2\text{N}$ refers to bis(trifluoromethylsulfonyl)amide. In the literature the term "amide" and "imide" are often used interchangeably, and in fact refer to the same ligand.

30 *Use of Mixtures of Room Temperature Ionic Liquids*

The electrolyte may comprise a combination of two different room temperature ionic liquids. These may be referred to as the "first" room temperature ionic liquid, which is based on a cation of Formula I, and an anion, and

35 the "second" room temperature ionic liquid. The second RTIL may be of any type, and therefore the cation component may be an ammonium cation, an imidazolium

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cation, a pyrrolidinium cation, a morpholinium cation, a pyridinium cation, a guanadinium cation, a piperidinium cation or a phosphorous-based derivative of the cations described above containing a nitrogen atom. According to 5 one suitable embodiment, the second RTIL also comprises a cation of Formula I, although the second RTIL overall must be of a different identity to the first RTIL.

The advantage of a mixture of RTILs in the electrolyte is 10 that the mixture will lower the melting point, thereby making the electrolyte more suitable for broader temperature range applications. In addition, a mixture may also enhance conductivity and, in some cases, electrochemical stability. As one example of a suitable 15 mixture, the combination of N-methyl-N-propyl-pyrrolidinium bis (trifluoromethanesulfonyl) amide and N-methyl-N-butyl-pyrrolidinium bis (trifluoromethanesulfonyl) amide is mentioned.

20 **Additives**

There are two main classes of additives that may be useful in the electrolyte of the present application. They are the solid electrolyte interphase-forming additives, and the gelling additives.

25

(a) Solid Electrolyte Interphase-forming Additives

The solid electrolyte interphase (SEI) is a surface formed on the lithium electrode in a lithium metal secondary cell. The SEI is a passivation layer that forms rapidly 30 because of the reactive nature of lithium metal. The SEI has a dual role:

1. It forms a passivating film that protects the lithium surface from further reaction with the electrolyte and/or contaminants.
- 35 2. The SEI acts as a lithium conductor that allows the passage of charge, as lithium ions, to and from the lithium surface during the charge/discharge cycling of a

- 15 -

lithium metal secondary cell.

The SEI is generally made up of a variety components. Usually, some "native" components are present due to 5 exposure to atmospheric contaminant at some point in the fabrication process. Once the cell has been fabricated, the electrolyte will usually react to form additional components in the SEI, which are reduction products of the electrolyte (which may be thought of as a solvent) and/or 10 salt. In some of the examples presented below, the RTIL consisted of $P_{1x}(Tf)_2N$. The spectroscopic evidence indicated that the SEI was formed from reduction products of the $(Tf)_2N^-$ anion. The reduction of just one component of the electrolyte appears to impart favourable cycling 15 properties to the lithium electrode in these electrolytes. However, the use of an additive consisting of selected components is predicted to contribute to the SEI, and therefore according to one embodiment a SEI-forming additive may be used.

20

SEI-forming additives may be selected from the group consisting of:

- polymers, including the electroconductive polymers, such as polyvinylpyrrolidone, polyethylene oxide, 25 polyacrylonitrile, polyethylene glycols, the glymes, perfluorinated polymers; and
- salts, preferably magnesium iodide, aluminium iodide, tin iodide, lithium iodide, tetraethylammonium heptadecafluoroctanesulfonate, dilithiumphthalocyanine, 30 lithium heptadecafluoroctanesulfonate, tetraethylammonium fluoride - tetrakis hydrogen fluoride.

(b) Gelling Additives

Gelling additives may be used to impart gel properties. 35 Gels may be considered to be "quasi-solids" as they have some structural properties, but retain the conductive properties of the liquid. Consequently gels are within

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the scope of the term "liquid" in the present application.

The gelling additives may be selected from inorganic particulate materials (sometimes referred to as 5 nanocomposites, being fine particulate inorganic composites). Amongst these, examples are SiO₂, TiO₂ and Al₂O₃.

Polymer or polymerizable monomer components may also be 10 used to gel the RTIL into an elastomeric material. Polymers useful for such a purpose include methylmethacrylate, dimethylaminoacrylamide and dimethylaminoethylacrylamide. Lithium polyelectrolyte salts can also be used for this purpose.

15

Counterion

The lithium ions are generally incorporated into the electrolyte by the addition of a lithium salt, consisting 20 of lithium ions and counterions, to the room temperature ionic liquid. Once added, the lithium ions and counterions dissociate, and are effectively a solute to the room temperature ionic liquid solvent. If the counterions are the same as the anion of the room temperature ionic liquid, then the lithium addition can be 25 considered to be doping of the electrolyte. In other words, doping can be considered as a cation substitution. Alternatively a different counterion can be used. The counterion can be within the classes (i) to (xiii) listed above for the anions, or may be any other counterion for 30 lithium, including polyanions. Generally, however, the counterion for the lithium will be one or more ions selected from classes (i) to (xiii).

The concentration of lithium (or dopant) can be between 35 0.01% and 90% of the overall material by weight, preferably between 1 and 49% by weight. It is generally simpler to refer to the lithium concentration of the

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electrolyte in moles of lithium ions per kilogram of total electrolyte, and in this unit the lithium is suitably present in an amount of from 0.01 to 2.0 mol/kg, preferably 0.1 - 1.5 mol/kg, and most preferably 0.2 - 0.6 mol/kg. The result is a liquid at room temperature in the cases of some members of the above salt families. In a most cases a liquid is generated over some temperature region.

10 **Organic Solvent**

The electrolyte may comprise any number of further components, one example being an organic solvent. Preferred organic solvents are water immiscible organic solvents. When present, the organic solvent may be used 15 in an amount of 0-90 wt%, preferably 10-70 wt%.

Preparation of the Electrolyte

The electrolytes described in the invention are preferably prepared by adding lithium salt to the room temperature 20 ionic liquid (or molten plastic crystal), mixing and drying under vacuum at elevated temperature. Preferably the electrolyte is then degassed, for example by contacting with a stream of dry argon, to remove dissolved gases and residual water.

25

Energy Storage Devices

The term energy storage device encompasses any device that stores or holds electrical energy, and encompasses batteries, supercapacitors and asymmetric (hybrid) 30 battery-supercapacitors. The term battery encompasses single cells.

Lithium based energy storage devices are ones that contain lithium ions in the electrolyte.

35

Lithium battery encompasses both lithium ion batteries and lithium metal batteries.

Lithium ion batteries and lithium metal batteries are well known and understood devices, the typical general components of which are well known in the art of the
5 invention.

Secondary lithium batteries are lithium batteries which are rechargeable. The combination of the electrolyte and negative electrode of such batteries must be such as to enable both plating/alloying (or intercalation) of lithium onto the electrode (i.e. charging) and stripping/de-alloying (or de-intercalation) of lithium from the electrode (i.e. discharging). The electrolyte is required to have a high stability towards lithium, for instance approaching ~0V vs. Li/Li⁺. The electrolyte cycle life is also required to be sufficiently good, for instance at least 100 cycles (for some applications), and for others, at least 1000 cycles.

20 **Secondary Lithium Batteries**

The general components of a secondary lithium battery are well known and understood in the art of the invention. The principal components are:
a battery case, of any suitable shape, standard or otherwise, which is made from an appropriate material for containing the electrolyte, such as aluminium or steel, and usually not plastic;
battery terminals of a typical configuration;
a negative electrode;
30 a positive electrode;
a separator for separating the negative electrode from the positive electrode; and
an electrolyte (in this case, the electrolyte described above).

35

The negative electrode comprises a metal substrate, which acts as a current collector, and a negative electrode

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material. The negative electrode material can be lithium metal, a lithium alloy forming material, or a lithium intercalation material; lithium can be reduced onto/into any of these materials electrochemically in the device.

5

The metal substrate underlying the lithium can be of importance in determining the cycle performance of the cell. This element may also have the role of current collector in the cell. The metal substrate may be any suitable metal or alloy, and may for instance be formed from one or more of the metals Pt, Au, Ti, Al, W, Cu or Ni. Preferably the metal substrate is Cu or Ni.

10
15
The negative electrode surface may be formed either in situ or as a native film. The term "native film" is well understood in the art, and refers to a surface film that is formed on the electrode surface upon exposure to a controlled environment prior to contacting the electrolyte. The exact identity of the film will depend on the conditions under which it is formed, and the term encompasses these variations. The surface may alternatively be formed in situ, by reaction of the negative electrode surface with the electrolyte. The use of a native film is preferred.

20
25

The positive electrode is formed from any typical lithium intercalation material, such as a transition metal oxides and their lithium compounds. As known in the art, transition metal oxide composite material is mixed with binder such as a polymeric binder, and any appropriate conductive additives such as graphite, before being applied to or formed into a current collector of appropriate shape.

30
35
Any typical separator known in the art may be used, including glass fibre separators and polymeric separators, particularly microporous polyolefins.

Usually the battery will be in the form of a single cell, although multiple cells are possible. The cell or cells may be in plate or spiral form, or any other form. The
5 negative electrode and positive electrode are in electrical connection with the battery terminals.

Other Devices

The high conductivity and high electrochemical stability
10 that have been noted in the deployment of these electrolytes in secondary lithium batteries, demonstrate that these same electrolytes will function well in energy storage devices such as supercapacitors and asymmetric (hybrid) battery-supercapacitor devices. For the
15 asymmetric device, one of the lithium battery electrodes (either the positive or the negative) is replaced with a supercapacitor electrode. For a supercapacitor, both lithium battery electrodes are replaced by supercapacitor electrodes. Supercapacitor electrodes, by comparison with
20 lithium battery electrodes, are relatively simple structures at which the interaction with the electrolyte is simply an electrostatic charging and discharging of the electrochemical double layer. Supercapacitors are also commonly known as electrochemical double-layer capacitors
25 (EDLCs). Suitable electrolytes for supercapacitors are, like those described here, electrolytes with high ionic conductivity and high electrochemical stability (large voltage range).

30 In its general form, a supercapacitor comprises:

- a device case;
- terminals for electrical connection;
- a negative electrode, which is generally composed of a mixture of conductive carbon and highly activated (high surface area) carbon which are bound to a metallic substrate (current collector);
- a positive electrode, which is generally composed of

- 21 -

- a mixture of conductive carbon and highly activated (high surface area) carbon which are bound to a metallic substrate (current collector);
- a separator for maintaining physical separation of
 - 5 the negative and positive electrode; and
 - the electrolyte as described herein.

The negative and positive supercapacitor materials and methods for manufacture are well known and understood in
10 the art of the invention.

Asymmetric (hybrid) battery-supercapacitors are devices in which one battery electrode is combined with one supercapacitor electrode to yield an energy storage device
15 which has properties that are intermediate between those of batteries and supercapacitors. In its general form, an asymmetric battery-supercapacitor comprises:

- a device case;
- terminals for electrical connection;
- 20 - a negative electrode;
- a positive electrode;
- a separator for maintaining physical separation of the positive and negative electricity; and
- the electrolyte as described herein,

25 wherein one of said negative electrode and positive electrode is a battery electrode, and the other electrode is a supercapacitor electrode.

The nature and composition of the battery and
30 supercapacitor electrodes are fully described above, and are of the form and composition well known in the art. If the negative electrode is a battery negative electrode, such as a lithium intercalation material or a lithium metal electrode, then the positive electrode is a supercapacitor positive electrode, typically a high surface area carbon electrode material bonded to a metal substrate. If the negative electrode is a supercapacitor

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electrode, typically a high surface area carbon electrode material bonded to a metal substrate, then the positive electrode is a battery electrode, such as one that contains a lithium intercalation material.

5

For supercapacitors, the electrolyte may contain some lithium ions, but need not do so. Accordingly, in this embodiment of the invention, the presence of lithium ions is optional.

10

Charging and Conditioning of Device

In the case of a lithium metal battery, the initial rate of deposition of lithium onto the substrate is also of importance in developing long cycle life batteries.

15

Preferably the initial deposition rate is less than 0.5 mAcm^{-2} and most preferably less than 0.25 mAcm^{-2} during at least a part of the charging stage of the device, battery or cell. The device battery or cell is suitably charged at this rate for a period of not less than 5 minutes during 20 the charging stage. Charge-discharge cycling can then take place at a higher rate.

25

Conditioning is a method used to influence the surface properties of the electrodes, and particularly the negative electrode. The device, battery or cell is suitably conditioned by subjecting the device, battery or cell to successive discharging and recharging steps, wherein the recharging is conducted at a rate of less than 0.5 mAcm^{-2} (preferably less than 0.25 mAcm^{-2}) for at least a 30 part of the recharging stage. Preferably that period is not less than 5 minutes duration.

Examples

The present invention will now be described in further detail with reference to the following non-limiting Examples.

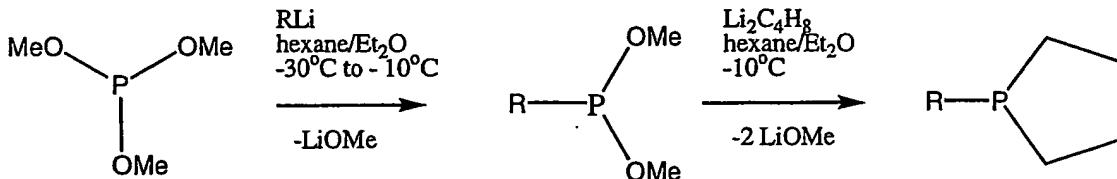
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*Materials and Preparation**Room Temperature Ionic Liquids*

Room temperature ionic liquids containing X=N in the ring structure were prepared in accordance with the procedure described in MacFarlane et al. "Pyrrolidinium Imides: a New Family of Molten Salts and Conductive Plastic Crystal Phases", *Journal of Physical Chemistry B*, 103 (99) 4164-4170.

15

The preparation of the phospholanium salts (X=P) requires the synthesis of a phospholane precursor, although it is noted that the six-membered phosphorinane and the corresponding phosphorinanium salt could be prepared. The phospholane precursor can be synthesised from trimethylphosphite according to the scheme outlined below, as described by Emrich and Jolly.[1]

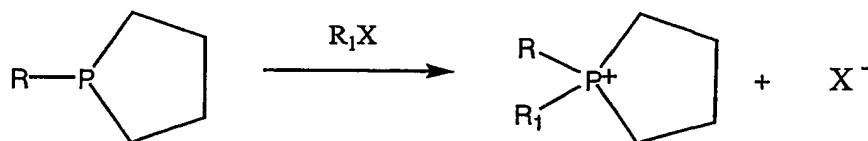


25 Alternative methods could be used, involving, for example, the reduction of phospholane oxide with phenylsilane,[2] the simultaneous addition of a bis-Grignard reagent and benzothiadiphosphole,[3] or the reaction of aluminacyclopentanes in the presence of Cp_2ZrCl_2 catalyst, 30 copper halides and dichloroalkylphosphine.[4]

The phospholane can be converted to a quaternary phosphonium species through reaction with the appropriate

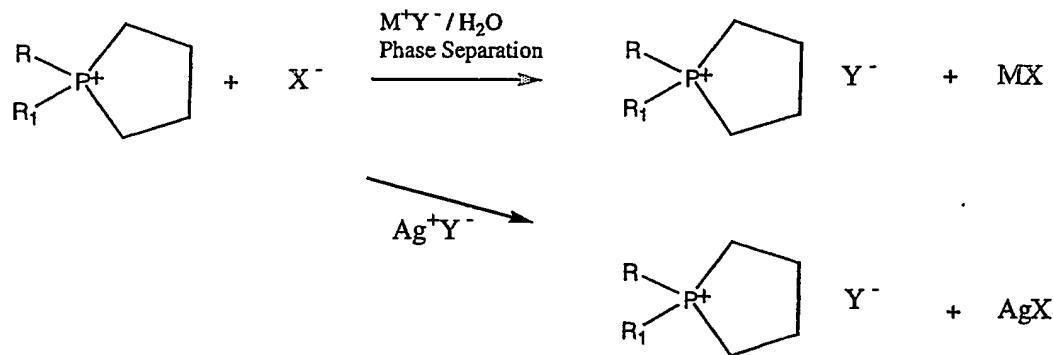
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alkyl halide (alkylation) to form the alkyl phospholanium halide salt, as shown below (where X is a halide e.g., I⁻, Br⁻, Cl⁻ etc.):



5

The RTIL can be obtained from the halide precursor by metathesis, with the route being dictated by the relative solubility of the product and by-product. For example, a hydrophobic product (e.g., using Li(Tf)₂N) can be obtained
10 by metathesis in aqueous solution, and the product is insoluble in water.[5] Alternatively a hydrophilic product can be obtained by metathesis with a silver salt (e.g., AgDCA) in aqueous solution. The insoluble by-product (e.g., AgI) is removed by filtration and the product is
15 obtained by the evaporation of water at reduced pressure.[6,7]



Similarly, As analogues may be prepared according to Reference[8].

20

1. P. Emrich and P. W. Jolly, *Synthesis*, 1, 39 (1993).
2. K. L. Marsi, *J. Am. Chem. Soc.*, 91, 4724 (1969).
3. G. Baccolini, C. Boga and U. Negri, *Synlett*, 2000, 1685 (2000).
- 25 4. U. M. Dzhemilev, A. G. Ibragimov, R. R. Gilyazev and

- 25 -

- L. O. Khafizova, *Tetrahedron*, 60, 1281 (2004).
5. D. R. MacFarlane, P. Meakin, J. Sun, N. Amini and M. Forsyth, *J. Phys. Chem. B*, 103, 4164 (1999).
6. D. R. MacFarlane, J. Golding, S. Forsyth, M. Forsyth
5 and G. B. Deacon, *Chemical Communications* 1430 (2001).
7. J. Golding, S. Forsyth, D. R. MacFarlane, M. Forsyth
and G. B. Deacon, *Green Chemistry*, 4, 223 (2002).
8. J.B. Lambert and H. Sun *J. Org. Chem.* 42, 1315 (1977).

10 **Electrolytes**

These were prepared by adding the required amount of the dried lithium salt specified in the example (available commercially) to the required amount of room temperature ionic liquid. The lithium salt was allowed to dissolve at 15 50°C overnight. Unless otherwise stated, the counterion to lithium in the lithium salt is the anion of the room temperature ionic liquid.

Battery-like cells

20 'Battery' like cells were fabricated using resealable stainless steel cells which were developed in-house, as illustrated in Figure 1. The basic design incorporated a case 1, electrodes 2a and 2b, a separator 3 incorporating electrolyte, polypropylene sleeves 4, a socket head screw 25 5, and a Teflon gasket 6 to seal, and electrically isolate, the two halves of the cell. Stack pressure in the cell was maintained by means of a spring 7, which applied ~1 kgcm⁻² stack pressure perpendicular to the electrode surface.

30

The lower electrode 2b was generally the lithium electrode. This was formed from lithium metal foil (Aldrich 99.9 % - thickness 180 µm), which was washed with hexane and brushed with a polyethylene brush. The positive 35 electrode 2a was prepared by coating a foil (either aluminium or platinum) with an active material formulation. The active material (AM), was either LiCoO₂ or

- LiMn_2O_4 . The electrode coating was prepared by weighing the components in the following ratios; - AM - 80%, Graphite (KS_4) - 7%, Carbon Black - 3%, PVdF - 10%. The solid components were mixed in a mortar and pestle and a
- 5 quantity of dimethylacetamide (DMAc ~130%) was added slowly with mixing to form a slurry. The slurry was transferred to a beaker and heated (low heat) with constant stirring until the mixture had reached the correct consistency. The slurry was then applied to the
- 10 current collector (aluminium or platinum) using the doctor blade technique. The resulting coated foil was then dried at 60 °C for several hours prior to drying under vacuum at 60 °C for greater than 24 hours.
- 15 Glass fibre mats or microporous polyolefin sheets were cut to size and used as the separators.

The cells were assembled (in an Argon glovebox) by placing an electrode 2b in the case 1, adding a separator 4

20 (already wetted with electrolyte) and by finally placing the second electrode 2a. The cells were sealed in the glovebox and could then be removed for testing.

3-electrode cells

- 25 The electrochemical measurements were performed in a 3-electrode cell 8, consisting of a platinum (or copper) working electrode (WE) 9, a lithium quasi-reference electrode (RE) 10, and a lithium counter electrode (CE) 11. The cell is shown schematically in Figure 2.
- 30 For the cyclic voltammetry measurements the potential (vs. Li/Li^+) was scanned from 2000 mV to -500 mV and back to 2000 mV at a rate of 100 mVs^{-1} . The current response of the working electrode was recorded throughout the experiment.
- 35 At low potentials (< ~0 mV vs. Li/Li^+), Li^+ is reduced to Li(s) and is deposited on the electrode producing a negative current (corresponding to charging a Li metal

cell). When the scan is reversed and the potential rises above ~ 0 mV (vs. Li/Li⁺) Li(s) is oxidised to Li⁺ (dissolution), producing a positive current (corresponding to discharging a Li metal cell). Integrating the curves 5 provides a measure of the amount of charge deposited (reduced Li⁺) and the amount of charge stripped (oxidised Li(s)). In this case the ratio of [oxidised Li(s) reduced Li⁺] provides a measure of the efficiency of the deposition/dissolution process. An efficiency of less than 10 100% indicates that the deposited lithium has reacted with the electrolyte and/or contaminants to produce a product that is not electrochemically reversible.

Cycling efficiency measurements

15 The cycling efficiency measurements were made using the 3-electrode cell described above. A deposit of lithium was galvanostatically plated onto the surface of the working electrode followed by cycling of a fraction of the original excess. The number of cycles required to consume 20 the original excess (indicated by a sharp change in dissolution potential) was used to calculate the 'average cycling efficiency' of the electrolyte. All cycling efficiency values were determined at 50°C in ~0.5 mL of electrolyte. The cycling efficiency is defined by:

25

$$\text{Avg. Cyc. Eff.} = 100 \times NQ_{ps} / (NQ_{ps} + Q_{ex}) \quad [2]$$

where N is the number of cycles, Q_{ex} is the plated excess (1 Ccm⁻²) and Q_{ps} is the cycled fraction (0.25 Ccm⁻²). In 30 the following experiments, references to a charge density of 1.0 Ccm⁻² refers to the plated excess, and it will be understood that the cycled fraction is 0.25 Ccm⁻² if not otherwise stated. Such experiments also serve to show the behaviour of the ionic liquid in the practical situation 35 of a cell designed to have a coulombic excess of Li in the negative electrode as compared to the capacity of the positive electrode.

Example 1

The electrochemical stability of a 0.5 mol/kg lithium bis(trifluoromethanesulfonyl)amide in methyl butyl pyrrolidinium bis (trifluoromethanesulfonyl)amide on a lithium electrode deposited on to a Ni substrate is determined by cyclic voltammetry using the 3-electrode cell described above (with Ni working electrode). The test was conducted at 100 mVs⁻¹ and at ambient temperature.

10 The results of the test are illustrated in Figure 3. High reversibility is observed, with no indication of degradation of the electrolyte.

Example 2

15 To show the ability of the electrolyte to reversibly cycle lithium a cycling efficiency experiment was conducted. A solution of 0.5 mol/kg lithium bis(trifluoromethanesulfonyl)amide in methyl butyl pyrrolidinium bis (trifluoromethanesulfonyl)amide was made up and a cycling efficiency experiment carried out at 0.25 mAcm⁻² and 1 Ccm⁻² (0.25 Ccm⁻² cycled fraction) on a Pt electrode at 50°C. The electrode cycles for 63 cycles (Figure 4), indicating a cycling efficiency of 94.0 %.

25 **Example 3**

The test of example 2 is repeated on a platinum substrate at the higher rate of 1.0 mAcm⁻² and 1 Ccm⁻² (0.25 Ccm⁻² cycled fraction). The electrode cycles for 430 cycles (Figure 5), indicating a cycling efficiency of 99.1 %.

30 Because of the large number of cycles, only the maximum deposition (reduction) and dissolution (oxidation) potentials for each cycle are shown.

Example 4

35 To show the influence of current density (charge/discharge rate), the test of examples 2 and 3 are repeated using varying current densities on Pt. Cycling efficiencies are

shown in Figure 6. These indicate the presence of an upper limit in current density beyond which dendritic deposition morphology occurs.

5 **Example 5**

To show the influence of a different substrate, the platinum substrate was substituted with a copper substrate and the test of example 2 repeated with the new substrate. The test was conducted at 0.25 mAcm^{-2} and 1 Ccm^{-2} (0.25 Ccm^{-2} cycled fraction). The electrode cycles for 9 cycles (Figure 7) indicating a cycling efficiency of greater than 69.2 %.

Example 6

15 To demonstrate high efficiency on the copper substrate a cycling efficiency experiment was performed at a low rate. The test of example 2 is carried out on a copper substrate at 0.1 mAcm^{-2} and 1 Ccm^{-2} . The electrode cycles for 330 cycles (Figure 8) indicating a cycling efficiency of greater than 98.8 %.

Example 7

25 To demonstrate the effect of prior cycling (conditioning) at low rates, the conditions and materials of example 6 are repeated except that after cycling at the proscribed rates (0.1 mAcm^{-2}) for 330 cycles, the rates are increased sequentially (0.25 mAcm^{-2} - Fig. 9a, 0.5 mAcm^{-2} - Fig. 9b). A cycling efficiency in excess of 99% is obtained.

30 **Example 8**

To demonstrate the use of another derivative of the pyrrolidinium series a solution of 0.5 mol/kg lithium bis(trifluoromethanesulfonyl)amide in methyl propyl pyrrolidinium bis (trifluoromethanesulfonyl)amide was made up and a cycling efficiency experiment carried out at 1.0 mAcm^{-2} and 1 Ccm^{-2} on a Pt electrode at 50°C . The electrode cycles for 44 cycles (Figure 10), indicating a cycling

- 30 -

efficiency of 91.7 %.

Example 9

The cycling efficiency test generally outlined in example 2 was repeated with changes made to the electrolyte used, additive, lithium salt, salt concentration and/or temperature, combined with the current density outlined in the table. For all experiments a copper substrate was used, and the room temperature ionic liquid was methyl propyl pyrrolidinium bis(trifluoromethanesulfonyl)amide, unless indicated in the left-hand column. Unless otherwise specified in the left-hand column of the table, the lithium salt used was lithium bis(trifluoromethanesulfonyl)amide. The lithium ion (lithium salt) concentration was 0.5 mol/kg unless otherwise stated in brackets in the left column of the table. The results are summarised below.

Additive or details of variation	Temp . (°C)	Rate mAcm ⁻²	Number of cycles			Cyc. Eff. (%)	
			1	2	3	Av.	Max.
PEO (MW 100000 0.2 wt%)	50	1.0	9	35	21	84.4	89.7
PVP (MW 40000 0.15 wt%)	50	1.0	27	14	10	81.0	87.1
Tetraglyme (0.2 wt%)	50	1.0	9	5	10	66.7	71.4
SiO ₂ (5wt%)	50	1.0	5	5	3	52.0	55.6
SiO ₂ (5wt%)	50	0.5	20			83.3	83.3
MgI ₂ (1000ppm)	50	1.0	4			50.0	50.0
MgI ₂ (500ppm)	50	1.0	15	7	10	72.7	78.9
MgI ₂ (100ppm)	50	1.0	6	9		64.6	69.2

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MgI_2 (100ppm)	50	0.5	26	9		78.0	86.7
Variation of Li salt or room temperature ionic liquid examples follow:							
$LiPF_6$ (0.5 molkg ⁻¹)	50	1.0	<1			<20.0	<20.0
$LiPF_6$ (0.5 molkg ⁻¹)	50	0.5	3	6	3	48.5	60.0
$LiAsF_6$ (0.5 molkg ⁻¹)	50	1.0	1			20.0	20.0
$LiAsF_6$ (0.5 molkg ⁻¹)	50	0.5	43	36	26	89.7	91.5
$LiAsF_6$ (1.0 molkg ⁻¹)	50	0.5	61			93.8	93.8
$Li(Tf)_2N$ (0.5 molkg ⁻¹)	75	1.0	7	4	5	57.1	63.6
$Li(Tf)_2N$ (1.0 molkg ⁻¹)	50	1.0	10			74.2	74.2
$Li(Tf)_2N$ (1.0 molkg ⁻¹)	75	1.0	13			76.5	76.5
$LiAsF_6$ (1.0 molkg ⁻¹)	75	1.0	49	51		92.6	92.7
$LiAsF_6$ (1.5 molkg ⁻¹)	100	0.5	36	33		89.6	90.0
$LiAsF_6$ (1.5 molkg ⁻¹)	125	1.0	28			87.5	87.5
$Li(Tf)_2N$ (0.5 molkg ⁻¹) in $P_{13}(Tf)_2N:P_{14}(Tf)_2N$ (1:1)	50	1.0	11			73.3	73.3

It will be noted that the final example in the table

involves the use of a 1:1 mixture of two different room temperature ionic liquids. The physical properties of this mixture and other mixtures of two room temperature ionic liquids makes mixtures an attractive proposition for
5 commercial application.

Example 10

The electrolyte used in Example 1 was incorporated into a cell as illustrated in Figure 1. The cell incorporated a
10 lithium negative electrode, a 0.5 molkg^{-1} $\text{Li}(\text{Tf})_2\text{N}/\text{P}_{14}(\text{Tf})_2\text{N}$ electrolyte, a Celgard™ separator and a LiMn_2O_4 positive electrode on an aluminium current collector. The cell was cycled at the C/10 rate (i.e., 10 hours to charge/discharge) at 50°C. The results of the cycling of
15 this cell are presented in Figure 11.

Example 11

The electrolyte used in Example 8 was incorporated into the cell as illustrated in Figure 1. The cell incorporated a
20 lithium negative electrode, a 0.5 molkg^{-1} $\text{Li}(\text{Tf})_2\text{N}/\text{P}_{13}(\text{Tf})_2\text{N}$ electrolyte, a glass fibre separator and a LiMn_2O_4 positive electrode on an platinum current collector. The use of a platinum current collector for the positive electrode improves the capacity retention. The
25 cell was cycled at the C/10 rate (i.e., 10 hours to charge/discharge) at 80 °C. The results of the cycling of this cell are presented in Figure 12.

Example 12

30 The cell of Example 11 was modified by substituting the LiMn_2O_4 positive electrode with a LiCoO_2 positive electrode. The cell incorporated a lithium negative electrode, a 0.5 molkg^{-1} $\text{Li}(\text{Tf})_2\text{N}/\text{P}_{13}(\text{Tf})_2\text{N}$ electrolyte, a glass fibre separator and a LiCoO_2 positive electrode on
35 an platinum current collector. The cell was cycled at the C/10 rate (i.e., 10 hours to charge/discharge) at 80 °C. The results of the cycling of this cell are presented in

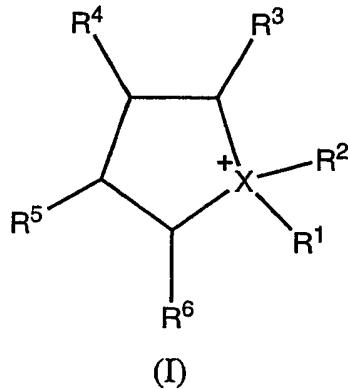
Figure 13.**Example 13**

The electrochemical stability of phosphonium based RTILs
5 is indicated by example 13. In this example a room
temperature ionic liquid comprising a phosphonium cation
with three n-butyl groups, a single n-hexadecane chain and
xylene sulfonate anion ($P_{44416}XS$) was used. The phosphonium
based RTIL was tested in the 3-electrode cell, using a
10 platinum working electrode, glassy carbon counter
electrode and a silver quasi-reference electrode. The
test was conducted at $100mVs^{-1}$ at 100°C . The results are
presented in Figure 14. This figure shows that electrode
exhibits minimal current response over a 10V range,
15 indicating sufficient stability for application in an
electrochemical device such as a rechargeable lithium
cell.

It will be understood to persons skilled in the art of the
20 invention that the examples outlined above are
illustrative only, and many modifications may be made
without departing from the spirit and scope of the
invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An electrolyte for use in an energy storage device, the electrolyte comprising a room temperature 5 ionic liquid of:
- (i) a cation of Formula I:



in which X is N, P or As

- 10 R¹ is alkyl or a fully or partially halogenated alkyl; R² is alkyl or a fully or partially halogenated alkyl; R³ to R⁶ are each independently H, alkyl, halo, fully or partially halogenated alkyl, nitrile, alkyl substituted by nitrile or heteroatom, or any other group; and
- 15 (ii) an anion;
together with
(iii) lithium ions.

2. The electrolyte of claim 1, wherein R³ to R⁶ are 20 each H or halo.

3. The electrolyte of claim 1 or claim 2, wherein R¹ is methyl or partially or fully halogenated methyl.

- 25 4. The electrolyte of any one of claims 1 to 3, wherein X is N.

5. The electrolyte of any one of claims 1 to 4,

wherein the cation is not halogenated.

6. The electrolyte of any one of claims 1 to 5, wherein the room temperature ionic liquid is selected from
5 the group consisting of:
- (a) salts of cations of Formula I in which R² is iso-propyl or an alkyl of 4 or more cations, and an anion;
- (b) salts of cations of Formula I in which R² is methyl, ethyl or propyl, with an anion selected from the group
10 consisting of:
- (i) perfluorinated alkyl fluorides of boron
- (ii) Halides, alkyl halides perhalogenated alkyl halides of group VA(15) other than PF₆⁻
- (iii) C_xY_{2x+1}SO₃⁻ where x = 2 to 6 and y = F or H
- 15 (iv) sulfonyl amides, with the proviso that when the sulfonyl amide is a perfluorinated bis amide, the perfluorinated bis amide is of the formula (C_xY_{2x+1}SO₂)₂⁻ where x = 3 to 6 and y = F
- (v) C_xF_{2x+1}COO⁻, where x is as defined above
- 20 (vi) sulfonyl and sulfonate compounds other than those of group (iv) above, including aromatic sulfonates
- (vii) cyano group containing anions and cyanamide compounds including cyanide, dicyanamide and tricyanamide
- 25 (viii) Succinamide and perfluorinated succinamide
- (ix) Ethylendisulfonylamide and its perfluorinated analogue
- (x) SCN⁻
- 30 (xi) Carboxylic acid derivatives, including C_xH_{2x+1}COO⁻
- (xii) where x is as defined above
- (xiii) Weak base anions
- (xiv) Halide ions
- 35 (c) salts of cation of Formula I which are partially or fully halogenated, and an anion;
- (d) salts of cations of Formula I where X is P and an

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anion; and

- (e) a mixture of two different cations of Formula I with one or more anions.

7. The electrolyte of any one of claims 1 to 5,
5 wherein R² is an alkyl of 2 or more carbon atoms, or a partially or fully halogenated alkyl of 2 or more carbon atoms.

8. The electrolyte of claim 7, wherein R² is an
10 alkyl of 4 or more carbon atoms, or a partially or fully halogenated alkyl of 2 or more carbon atoms.

9. The electrolyte of any one of claims 1 to 5,
wherein R² is butyl, or partially or fully halogenated
15 butyl.

10. The electrolyte of claim 1, wherein the anion is selected from the group consisting of:

- (i) BF₄⁻ and perfluorinated alkyl fluorides of boron
20 (ii) Halides, alkyl halides or perhalogenated alkyl halides of group VA(15)
(iii) C_xY_{2x+1}SO₃⁻ where x = 0 to 6 and y = F or H
(iv) sulfonyl amides, including the bis amides and perfluorinated versions thereof
25 (v) C_xF_{2x+1}COO⁻, where x is as defined above
(vi) sulfonyl and sulfonate compounds, including aromatic sulfonates
(vii) cyano group containing anions and cyanamide compounds including cyanide, dicyanamide and tricyanamide
30 (viii) Succinamide and perfluorinated succinamide
(ix) Ethylenedisulfonylamide and its perfluorinated analogue
(x) SCN⁻
(xi) Carboxylic acid derivatives, including C_xH_{2x+1}COO⁻
35 where x is as defined above
(xii) Weak base anions
(xiii) Halide ions.

11. The electrolyte of claim 10, wherein the anion is selected from the group consisting of:

- (i) BF_4^- and perfluorinated alkyl fluorides of boron
- 5 (ii) Halides, alkyl halides or perhalogenated alkyl halides of group VA(15)
- (iii) $\text{C}_x\text{Y}_{2x+1}\text{SO}_3^-$ where $x = 0$ to 6 and $y = \text{F}$ or H ;
- (iv) sulfonyl amides, including the bis amides and perfluorinated versions thereof; and
- 10 (vi) sulfonyl and sulfonate compounds, including aromatic sulfonates.

12. The electrolyte of claim 10, wherein the anion is selected from the group consisting of:

- 15 (i) perfluorinated alkyl fluorides of boron
- (ii) Halides, alkyl halides perhalogenated alkyl halides of group VA(15) other than PF_6^-
- (iii) $\text{C}_x\text{Y}_{2x+1}\text{SO}_3^-$ where $x = 2$ to 6 and $y = \text{F}$ or H
- (iv) sulfonyl amides, with the proviso that when the sulfonyl amide is a perfluorinated bis amide, the perfluorinated bis amide is of the formula $(\text{C}_x\text{Y}_{2x+1}\text{SO}_2)_2^-$ where $x = 3$ to 6 and $y = \text{F}$
- 20 (v) $\text{C}_x\text{F}_{2x+1}\text{COO}^-$, where x is as defined above
- (vi) sulfonyl and sulfonate compounds other than those of group (iv) above, including aromatic sulfonates
- 25 (vii) cyano group containing anions and cyanamide compounds including cyanide, dicyanamide and tricyanamide
- (viii) Succinamide and perfluorinated succinamide
- (ix) Ethylendisulfonylamide and its perfluorinated analogue
- 30 (x) SCN^-
- (xi) Carboxylic acid derivatives, including $\text{C}_x\text{H}_{2x+1}\text{COO}^-$ where x is as defined above
- (xii) Weak base anions
- 35 (xiii) Halide ions.

13. The electrolyte of any one of claims 1 to 12,

wherein the electrolyte comprises a second room temperature ionic liquid.

14. The electrolyte of claim 13, wherein the second
5 room temperature ionic liquid comprises a cation of
Formula I and an anion.

15. The electrolyte of any one of claims 1 to 14,
comprising a solid electrolyte interphase-forming
10 additive.

16. The electrolyte of claim 15, wherein the solid
electrolyte interphase-forming additive is selected from
the group consisting of:
15 - polymers, including polyvinylpyrrolidone,
polyethylene oxide, polyacrylonitrile, polyethylene
glycols, glymes, perfluorinated polymers; and
- salts, including magnesium iodide, aluminium iodide,
tin iodide, lithium iodide, tetraethylammonium
20 heptadecafluorooctanesulfonate, dilithiumphthalocyanine,
lithium heptadecafluorooctanesulfonate, tetraethylammonium
fluoride - tetrakis hydrogen fluoride.

17. The electrolyte of any one of claims 1 to 16,
25 comprising a gelling additive.

18. The electrolyte of claim 17, wherein the gelling
additive is selected from the group consisting of:
inorganic particulate materials, including SiO_2 , TiO_2 and
30 Al_2O_3 ; and polymers or polymerizable monomer components,
including methylmethacrylate, dimethylaminoacrylamide and
dimethylaminoethylacrylamide.

19. The electrolyte of any one of claims 1 to 18,
35 wherein the lithium ions are associated with a counterion.

20. The electrolyte of claim 19, wherein the

counterion is the same as the anion of the room temperature ionic liquid.

21. The electrolyte of claim 19, wherein the
5 counterion is different to the anion of the room temperature ionic liquid.

22. The electrolyte of any one of claims 1 to 21, wherein the lithium is present in an amount of from 0.01
10 to 2.0 mol/kg measured as moles of lithium per kilogram of total electrolyte.

23. The electrolyte of claim 22, wherein the lithium is present in an amount of from 0.1 to 1.5 mol/kg.
15

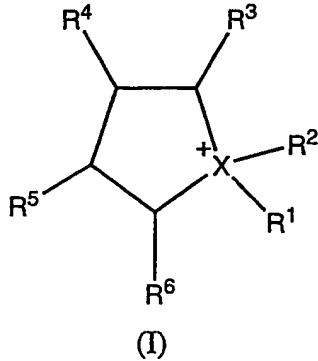
24. The electrolyte of claim 22, wherein the lithium is present in an amount of from 0.2 to 0.6 mol/kg.

25. The electrolyte of any one of claims 1 to 24,
20 comprising an organic solvent.

26. The electrolyte of claim 25, wherein the organic solvent is present in an amount of 0 - 90 wt%.

25 27. Use of a room temperature ionic liquid which is a salt of:

(i) a cation of Formula I:



- 40 -

in which X is N or P or As

R¹ is alkyl or a fully or partially halogenated alkyl;

R² is alkyl or a fully or partially halogenated alkyl;

R³ to R⁶ are each independently H, alkyl, halo, fully or

5 partially halogenated alkyl, nitrile, alkyl substituted by nitrile or heteroatom, or any other group; and

(ii) an anion; optionally together with

(iii) lithium ions

as an electrolyte for an energy storage device in which

10 the electrolyte is liquid at the temperature of use of the device.

28. Use of claim 27, wherein the storage device is a secondary lithium battery, supercapacitor or an asymmetric
15 battery-supercapacitor.

29. Use of claim 27, wherein the storage device is a secondary lithium battery, and the electrolyte contains lithium ions.

20

30. Use of claim 27, wherein the lithium based storage device is a lithium metal battery, and the electrolyte contains lithium ions.

25 31. Use of any one of claims 27 to 30, wherein the room temperature ionic liquid is selected from the group consisting of:

(a) salts of cations of Formula I in which R² is iso-propyl or an alkyl of 4 or more cations, and an anion;

30 (b) salts of cations of Formula I in which R² is methyl, ethyl or propyl, with an anion selected from the group consisting of

(i) perfluorinated alkyl fluorides of boron

(ii) Halides, alkyl halides perhalogenated alkyl
35 halides of group VA(15) other than PF₆⁻

(iii) C_xY_{2x+1}SO₃⁻ where x = 2 to 6 and y = F or H

(iv) sulfonyl amides, with the proviso that when the

- sulfonyl amide is a perfluorinated bis amide, the perfluorinated bis amide is of the formula $(C_xY_{2x+1}SO_2)_2$ where x = 3 to 6 and y = F
- (v) $C_xF_{2x+1}COO^-$, where x is as defined above
- 5 (vi) sulfonyl and sulfonate compounds other than those of group (iv) above,
- (vii) cyano group containing anions and cyanamide compounds including cyanide, dicyanamide and tricyanamide
- 10 (viii) Succinamide and perfluorinated succinamide
- (ix) Ethylendisulfonylamide and its perfluorinated analogue
- (x) SCN^-
- (xi) Carboxylic acid derivatives, including $C_xH_{2x+1}COO^-$ where x is as defined above
- 15 (xii) Weak base anions
- (xiii) Halide ions
- (c) salts of cation of Formula I which are partially or fully halogenated, and an anion;
- 20 (d) salts of cations of Formula I where X is P and an anion; and
- (e) a mixture of two different cations of Formula I with one or more anions.
- 25 32. An energy storage device comprising an electrolyte as claimed in any one of claims 1 to 26.
33. A secondary lithium battery comprising the electrolyte of any one of claims 1 to 26.
- 30 34. The secondary lithium battery of claim 33, wherein the electrolyte has high stability towards lithium.
- 35 35. The secondary lithium battery of claim 33 or claim 34, wherein the electrolyte has a cycle life of at least 100 cycles.

36. A secondary lithium battery comprising:

- (1) a battery case;
- (2) battery terminals;
- 5 (3) an negative electrode;
- (4) a positive electrode;
- (5) a separator for separating the negative electrode from the positive electrode; and
- (6) an electrolyte as claimed in any one of claims 1 to

10 26.

37. The secondary lithium battery of claim 36, wherein the negative electrode comprises a metal substrate and a lithium metal surface formed either in situ or as a
15 native film.

38. A method of charging the energy storage device of claim 32 or the battery of one of claims 33 to 36, comprising the step of charging at a charge rate of less
20 than 0.25 mAcm^{-2} during at least a part of the charging stage of the device or battery.

39. The method of claim 38, wherein the device or battery is charged at said rate for a period of not less
25 than 5 minutes during the charging stage.

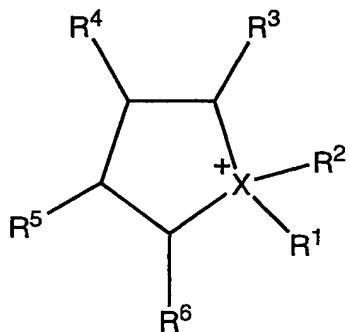
40. A method of conditioning the energy storage device of claim 32 or the battery of one of claims 33 to 36, comprising the steps of discharging the device or
30 battery and recharging the device or battery, wherein the recharging is conducted at a rate of less than 0.25 mAcm^{-2} for at least a part of the recharging stage.

41. The method of claim 40, wherein the recharging at
35 said rate of less than 0.25 mAcm^{-2} is conducted for a period of not less than 5 minutes.

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42. A supercapacitor comprising:

- a device case;
- terminals for electrical connection;
- a supercapacitor negative electrode;
- 5 - a supercapacitor positive electrode;
- a separator for maintaining physical separation of the negative electrode and the positive electrode; and
- an electrolyte comprising a cation of Formula 1:



(I)

10

in which X is N, P or As

- R¹ is alkyl or a fully or partially halogenated alkyl;
- R² is alkyl or a fully or partially halogenated alkyl;
- 15 R³ to R⁶ are each independently H, alkyl, halo, fully or partially halogenated alkyl, nitrile, alkyl substituted by nitrile or heteroatom, or any other group; and an anion.

43. An asymmetric battery-supercapacitor comprising:

- a device case;
- 20 - terminals for electric connection;
- a negative electrode;
- a positive electrode;
- a separator for maintaining physical separation of the negative electrode and the positive electrode; and
- 25 - the electrolyte of any one of claims 1 to 26; wherein one of said negative electrode and positive electrode is a battery electrode, and the other of said electrodes is a supercapacitor electrode.

- 44 -

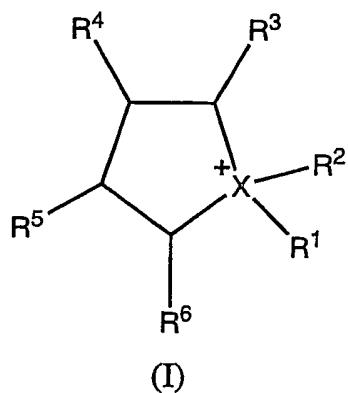
44. A method for preparing the electrolyte of any one of claims 1 to 26, adding lithium ions in the form of a salt to said room temperature ionic liquid, mixing and drying under vacuum at elevated temperature.

5

45. The method of claim 44, wherein the electrolyte is subjected to degassing.

46. Use of a room temperature ionic liquid
10 comprising:

(i) a cation of Formula I:

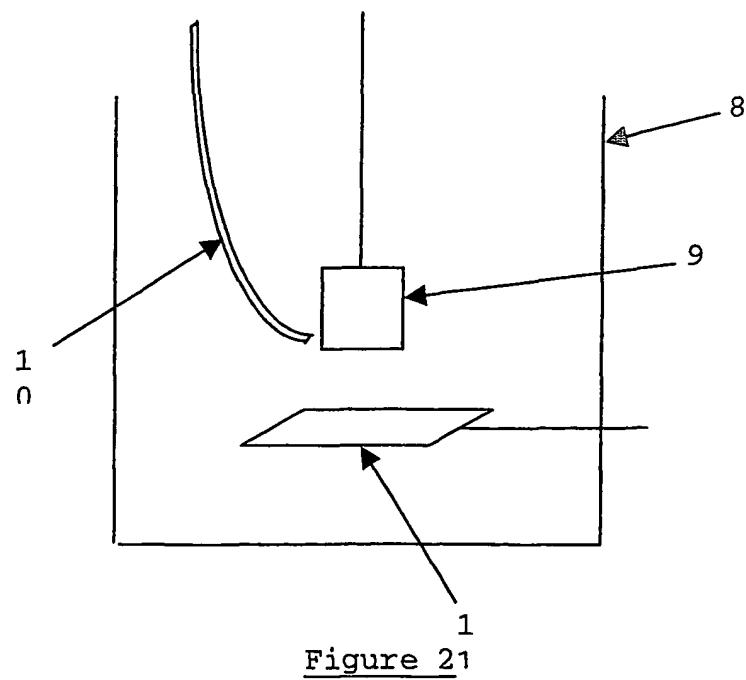
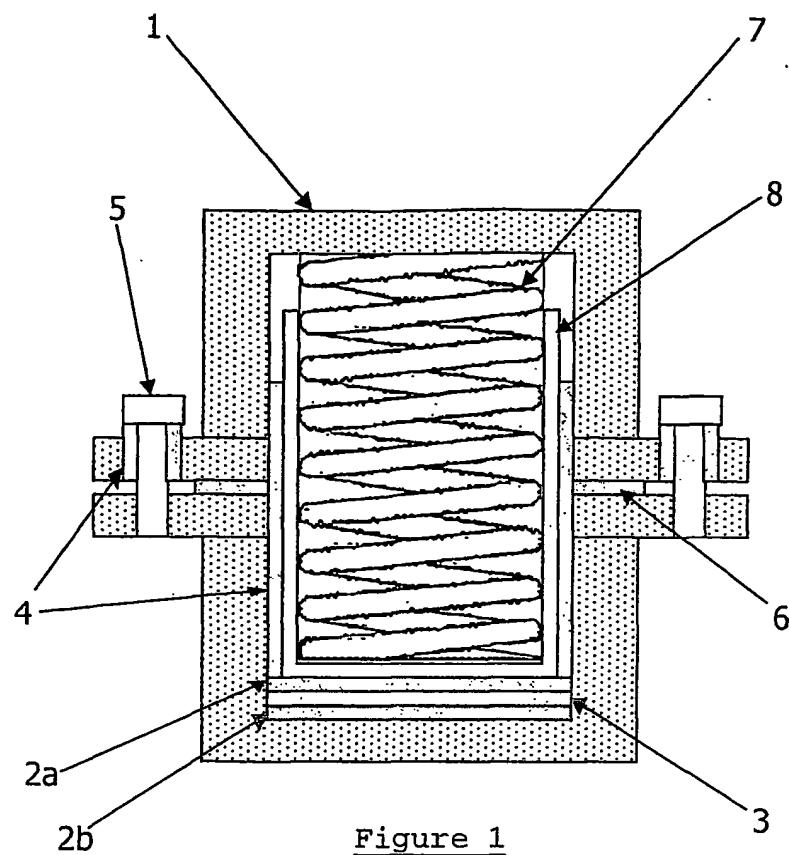


in which X is N, P or As

15 R^1 is alkyl or a fully or partially halogenated alkyl;
 R^2 is alkyl or a fully or partially halogenated alkyl;
 R^3 to R^6 are each independently H, alkyl, halo, fully or partially halogenated alkyl, nitrile, alkyl substituted by nitrile or heteroatom, or any other group; and

20 (ii) an anion;
as an electrolyte for an energy storage device in which the electrolyte is liquid at the temperature of use of the device.

- 1 -



- 2 -

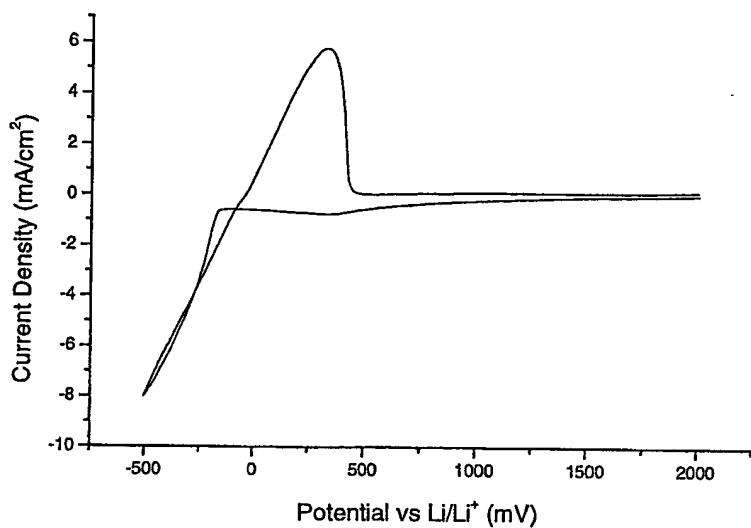


Figure 3

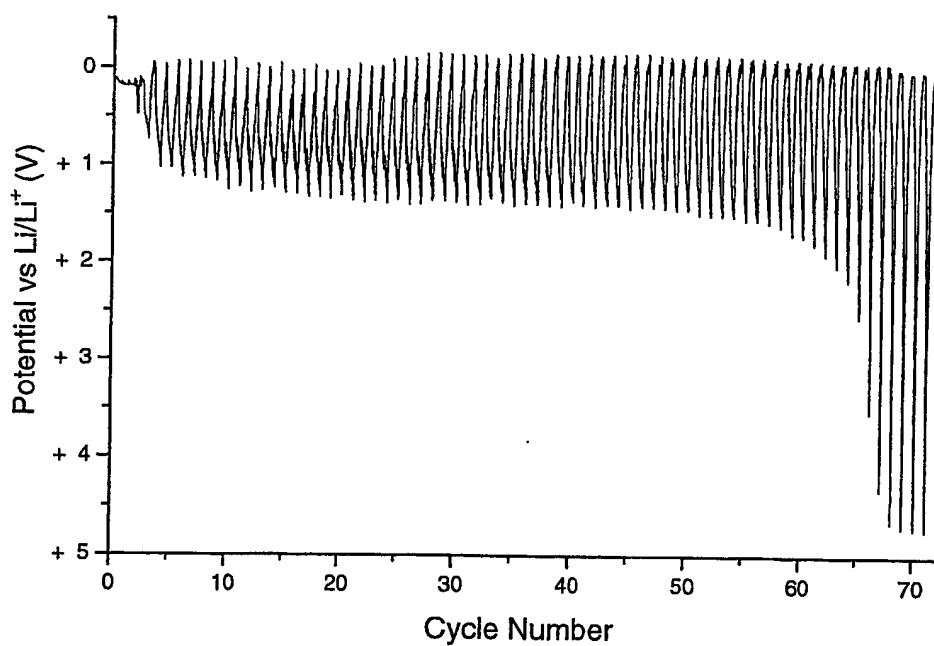


Figure 4

- 3 -

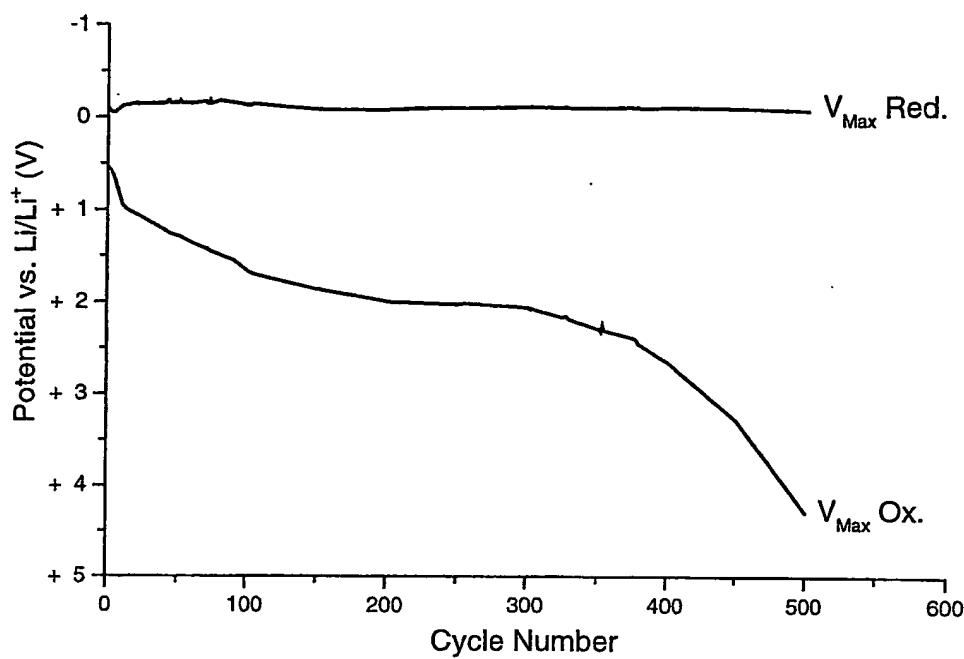


Figure 5

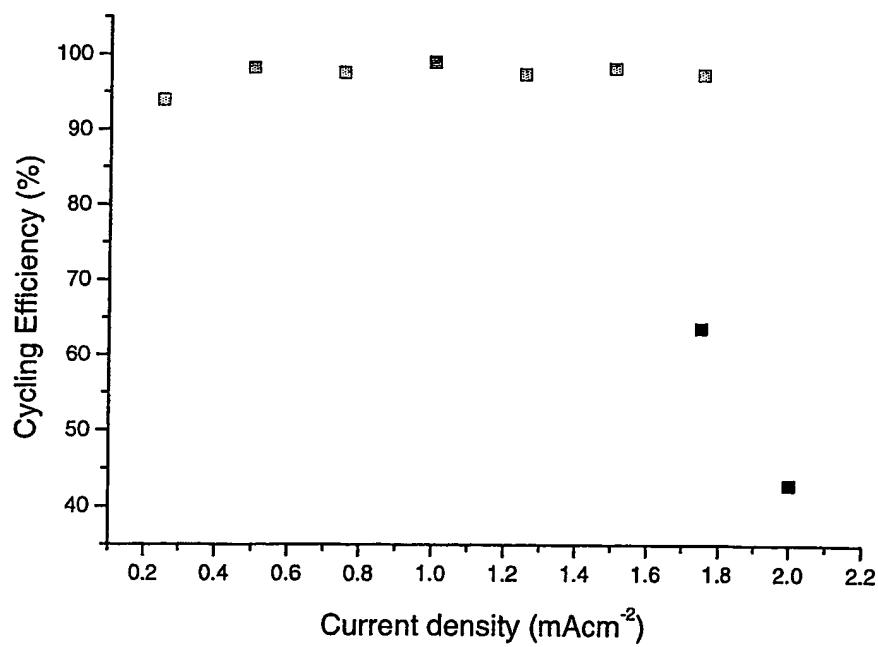


Figure 6

- 4 -

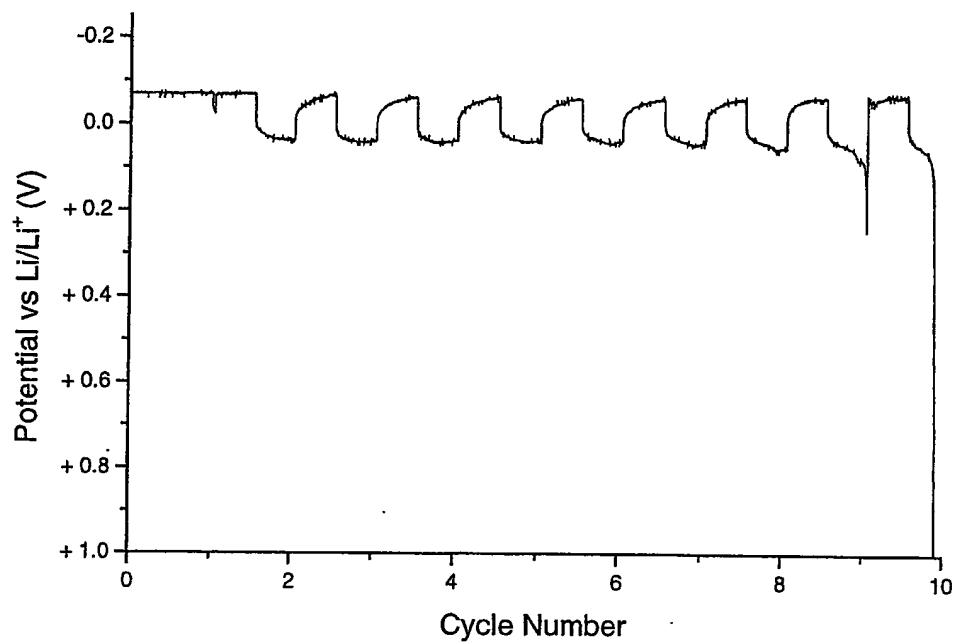


Figure 7

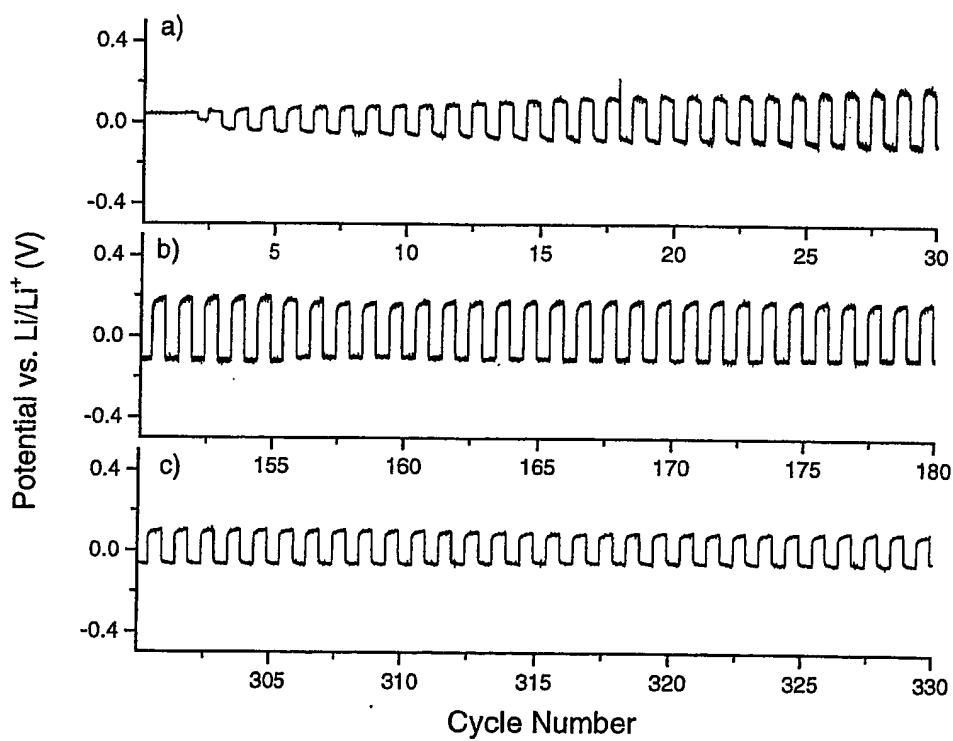


Figure 8

- 5 -

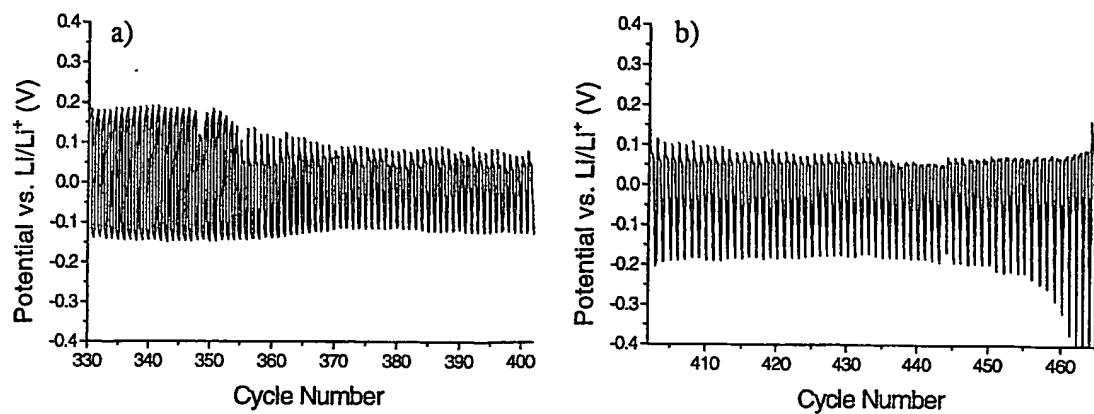


Figure 9

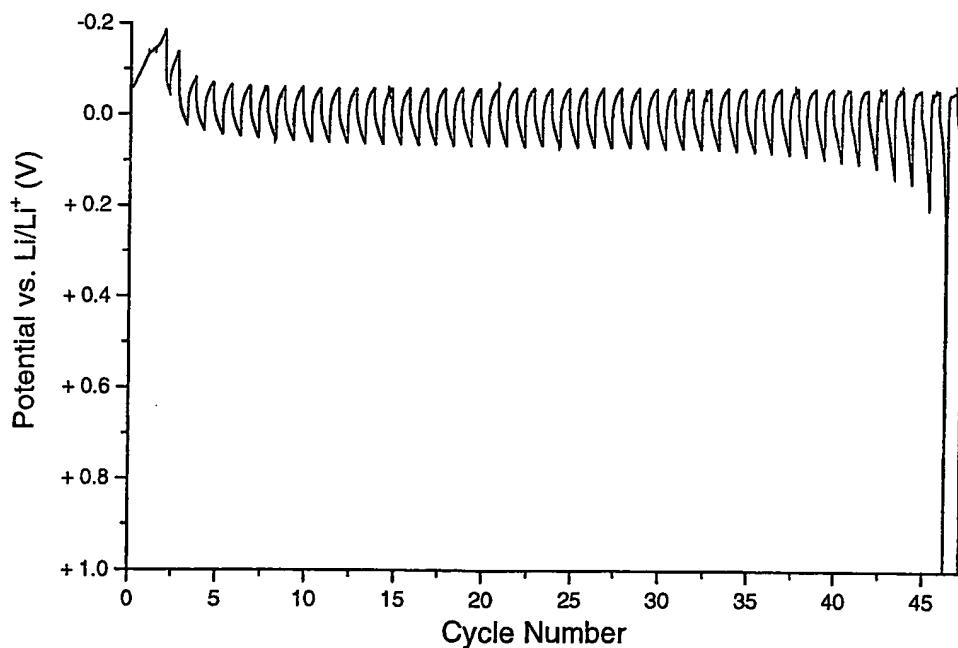


Figure 10

- 6 -

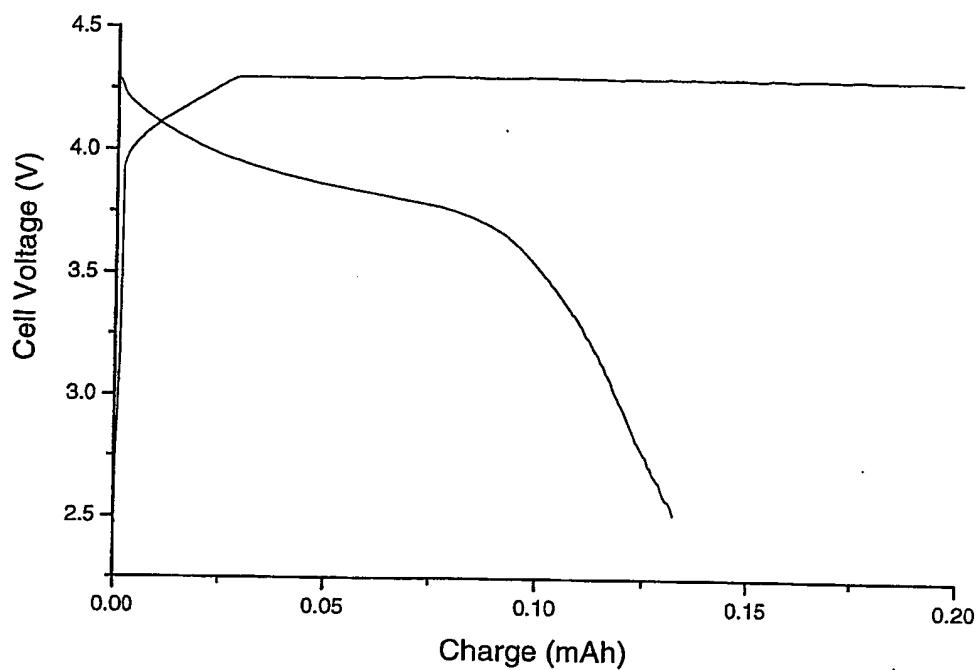


Figure 11

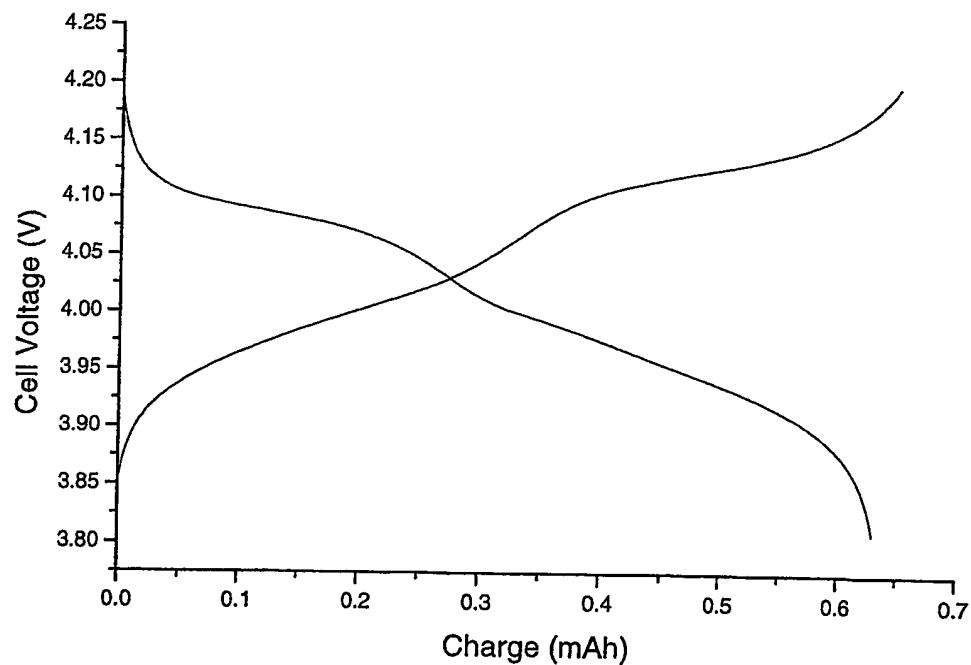


Figure 12

- 7 -

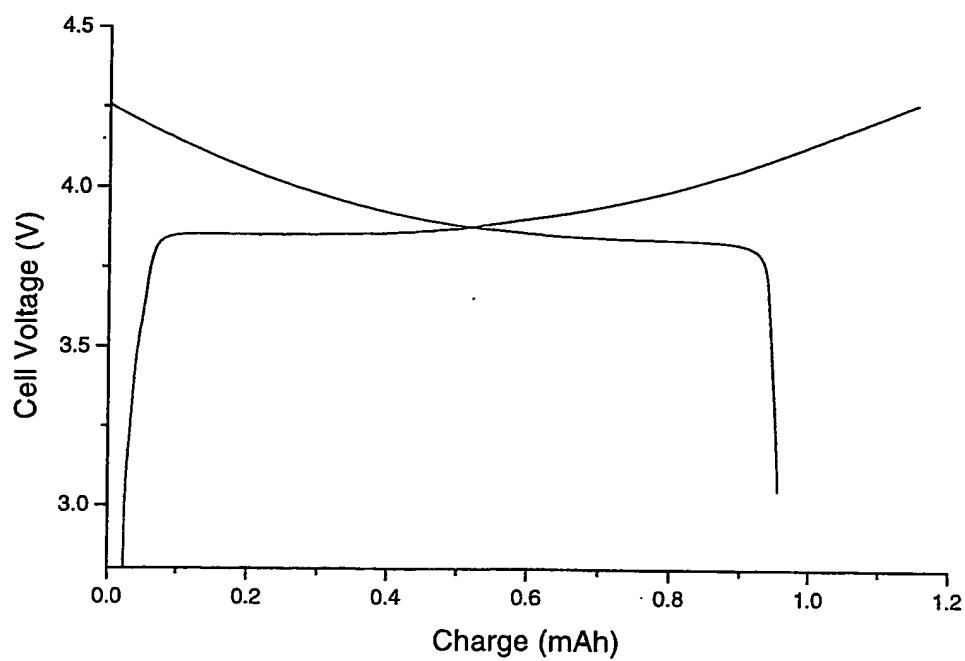


Figure 13

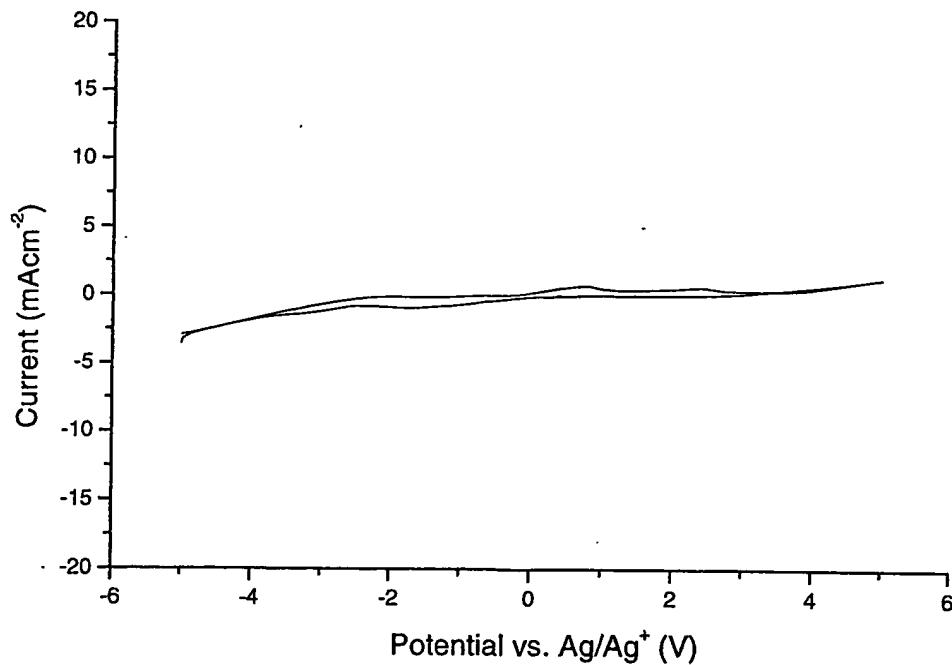


Figure 14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2004/000263

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.⁷: H01M 10/26, 10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC⁷ as above

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Derwent WPI: IPC⁷ as above and pyrrolid+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2002054515 A2 (University of Oklahoma) 11 July 2002 Whole Document	
A	US 20030003358 A1 (Mandal et al) 2 January 2003 Whole Document	
A	Derwent Abstract Accession No. 2002-733080/79, Class E19, L03 WO 2002082570 A1 (NEC Corporation) 17 October 2002 Abstract & Patent	
A	Derwent Abstract Accession No. 2003-819943/77, Class E13, L03, JP 2003-217655 A (Mitsubishi Chem Corp) 31 July 2003 Abstract & Patent	

Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents:		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the International search
2 April 2004

Date of mailing of the international search report

- 8 APR 2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2004/000263

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
WO	0254515				
US	2003003358	US	2002185459	US	2002190015
WO	02082570	EP	1381100	JP	2002304996
JP	2003217655				
END OF ANNEX					

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